IMPORTANCE OF THE POLARS AS INTERACTION MEDIUM WITH WATER DURING HYDROUS PYROLYSIS OF WOODFORD SHALE.

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INTRODUCTION

The thermal degradation of kerogen leads to the formation of a complex system in which gases, water, free hydrocarbons, polars and the residual kerogen are in close contact. The simulation of the formation of the bitumen wetted kerogen during artificial maturation allows to study the close interactions between the various phases formed. Previous studies have compared the influence of the reaction medium on the generation of hydrocarbons in hydrous pyrolysis conditions (where water is added to the sample) and confined pyrolysis (no water is added to the sample)[1,2]. These experiments could account for the effect of an external phase on the thermal evolution of type II kerogen. Other studies, (using a combination of pyrolysis and selective extractions) have focused on the role of internal media (free hydrocarbons, polars, residual kerogen) in the maturation processes and interactions with water during the maturation of type III organic matter[3,4]. The comparison between the two types of studies allows to precise the respective role of the organic reactants versus water in the chemical control of the organic system.

Although the role of liquid water is capital in hydrous pyrolysis, the role of the organic phases generated, the interactions between themselve and their interactions with water need still to be clarified. The following study aims to describe the reactivity of the organic system and its interactions with water in relation to the generation of hydrocarbons during hydrous pyrolysis of Woodford shale.

EXPERIMENTAL

The sample used is Woodford shale (WD26; 22%TOC; HI=401mgHC/gTOC, Tmax=427°C), collected in the Anadarko basin, Oklahoma. Powedered shale aliquots (10g) were loaded in stainless steel reactors (30cm^3 internal volume) pyrolyzed in the presence of 100 weight% water at temperatures between 260°C and 365°C for 3 days (temperature measurements were performed through an internal thermocouple in contact with the sample). Several maturation series were performed: 1) a reference series, called HP 2) a series called HPEC in which a same shale aliquot was treated the following way: pyrolysis at temperature T1, subsequent chloroform extraction; pyrolysis of the extracted sample at T2, subsequent chloroform extraction. This process was performed until 365°C. 3) a series called HPEP in which a same shale aliquot was treated the same way as for the HPEC series, but the extracting solvent was pentane.

In the HPEC and HPEP series, the same shale aliquot was repyrolyzed several times. Therefore, the pyrolysis time-temperature pair was compensated by TTI calculations in order to obtain maturation series that have reached TTI values identical to the reference series. However, for convenience, maturation scales are indicated in temperature and not in TTI, as far as the effective pyrolysis temperatures are not much different for all the series.

The samples were extracted either by hot chloroform or pentane for 45 minutes. No distinction was made between the expelled phase and the bitumen.

In order to quantify the polars yields and for further analysis of the solid residue, the samples of the HPEP series were also extracted by chloroform.

The asphaltenes were precipitated in hot heptane for 15 minutes and filtered. The maltene fraction was fractionned on alumina and silica micro-columns in resins, aromatics and saturates. All fractions were quantified.

PyGCMS was performed on chloroform extracted residues with a Pyroprobe CDS2000 connected to a HP5980 Series II Plus gas chromatograph coupled with a HP5972A mass spectrometer. The GC was equipped with a 60m DB-5 ms column initiallt held at 0°C for 5 min, then heated to 300°C at 5°C/min and held at 300°C for 15min.

RESULTS

Figure 1 shows the polars and aliphatics cumulated yields obtained for each series ·
as well as the non cumulated values for the HPEC series. The yields obtained with
the experimental procedures used have different meanings and therefore, some
values must be mathematically cumulated in order to allow comparisons. The
data for the reference series are always cumulative values, as far as the reactor is
loaded with a new shale aliquot at each pyrolysis step, and no mathematical
treatment needs to be done. For the HPEP series, the resins yields have been
cumulated and added to the non cumulated asphaltenes yields of each
experiment (asphaltenes are not removed from the sample at each pyrolysis step).

Up to T=300°C, Figure 1 shows similar values for the polars yields of the reference
and the cumulated HPEC series. The cumulated HPEC series on the contrary are
far stronger at T>300°C. The secondary cracking of the polars during hydrous
pyrolysis can be estimated from these data. The values for the reference series
decrease at T>300°C, while the polars generation potential of the kerogen is not
totally exhausted (there is a difference of about 55mg/g of rock between the
reference series and the cumulated HPEC series at 330°C). Therefore, it seems that
the « real » maximum bitumen generation occurs at 350°C and not 300°C as
shown by the maximum non cumulated yield of the HPEC series (occuring at
350°C) and the flatening of the HPEC cumulated curve. Howveer, additonnal
experiments at 310°C would be necessary in order to confirm this aspect. The
removal of the hydrocarbons and part of the resins by pentane extraction does not
modify the polars yields in the 260-300°C range as shown by Figure 1.

Figure 1 also shows the aliphatics yields for the reference series and the
cumulated values for the HPEC-HPEP series as well as the non cumulated values
for the HPEC series. At T>330°C, the cumulated aliphatic yields are far higher for
the HPEC series than for the others. In addition, the non cumulative aliphatic
yield for the HPEC series decreases, indicating that the kerogen alone is not able to
generate additional hydrocarbons. The HPEP series shows always the lowest
yields, even when cumulated.

As for the polars, the maximum aliphatic yield observed at 330°C is only
apparent. The HPEC series shows that the kerogen is able to generate
hydrocarbons up to 350°C. The low values for the HPEP series indicate that the
removal of the maltenes has a deleterious effect on the capacity of the
kerogen+asphaltenes assemblage to generate hydrocarbons.
It is difficult to estimate the secondary cracking of the aliphatics as far as 1) the
reference series includes the aliphatics generated by the kerogen and the polars,
while the HPEC series includes only the generation from the kerogen 2) the
generation of aliphatics from the kerogen+asphaltenes assemblage is modified by
the removal of the maltenes.

Table I and Figure II are respectively the Rock-Eval data and the PyGCMS
chromatograms of the chloroform extracted samples. Despite the different
pyrolysis conditions, these data are identical for all maturation series. This shows
that the kerogen itself is not much influenced by the removal of either the
polars+hydrocarbons or the maltenes.

DISCUSSION AND CONCLUSION

The use of the successive extraction-maturation series (HPEC and HPEP series)
allows to investigate the role of the bitumen as well as the maltenes on the
maturation of kerogen in hydrous conditions. The removal of the bitumen or the
maltenes at each maturation step does not influence the generation of the polars
from kerogen. It seems therefore that the polars and the hydrocarbons do not
have a great influence on the initial thermal breakdown of Woodford kerogen in
hydrous pyrolysis. As far as Lewan[5] reached similar conclusions through his
anhydrous versus hydrous pyrolysis conditions, it may be concluded that neither
the polars+hydrocarbons nor water influence the initial thermal breakdown of
the kerogen. This may support the idea that this stage resembles a
« depolymerization » process[6].

The situation is somewhat different when the generation of aliphatic hydrocarbons is considered. The removal of the bitumen (HPEC series) at each maturation step does not influence the aliphatic generation from the kerogen. However, the data show that the aliphatic generation from the kerogen is almost exhausted at T≥ 350°C. On the contrary, the aliphatic yield is strongly lowered in the HPEP series (removal of. the maltenes) whatever the temperature: the kerogen+asphaltenes assemblage yields less aliphatics than the kerogen alone (HPEC). This might be surprising as far as the polars content of the system decreases. Howveer, the decrease in polars is not counterparted by the generation of C_{15}^+ aliphatics. For Mahakam coal[4,5], such behavior has been attributed to crosslink reactions between the asphaltenes and the kerogen in the absence of the maltenes. However, the effect must be less important for Woodford kerogen in the conditions described here, as far as the Rock-Eval Tmax and the pyGCMS chromatograms are not modified (these parameters were strongly influenced in the experiments using Mahakam coal[4,5]).

These results suggest that the presence of liquid water is not the only necessary condition to allow the generation of aliphatics from the type II kerogen+asphaltenes assemblage. Indeed, water and the maltenes need to be present together in order to allow good conditions for aliphatics generation. As far as the kerogen alone yields higher amounts than the kerogen+asphaltenes assemblage, it is suggested that the maltenes in addition to water avoid the crosslink reactions of the asphaltenes with the kerogen during maturation

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TABLE I Rock-Eval data on raw Woodford Shale and on pyrolyzed samples HP: Hydrous pyrolysis reference series. HPEC successive pyrolysis- chloroform extraction series. HPEP successive pyrolysis- pentane extraction series. All samples chloroform extracted prior to Rock-Eval pyrolysis.

	HP		HPEC		HPEP	
Pyrolysis Temperature (°C)	Tmax (°C)	HI mgHC/gC	Tmax (°C)	HI mgHC/gC	Tmax (°C)	HI mgHC/gC
Raw Woodford Shale	427	401				
278	440	349	438	390	438	371
298	442	305	441	319	442	287
329	453	126	453	109	454	101
346	461	57	468	38	466	50
358	554	21	540	19	-	-

FIGURE 1 Polars and C_{15}^+ aliphatics yields for the HP, HPEC and HPEP series. Cumulated and non cumulated values as indicated. The reference series (HP) values are intrinsic cumulative data as far as a new shale aliquot is loaded in the reactor at each pyrolysis temperature.
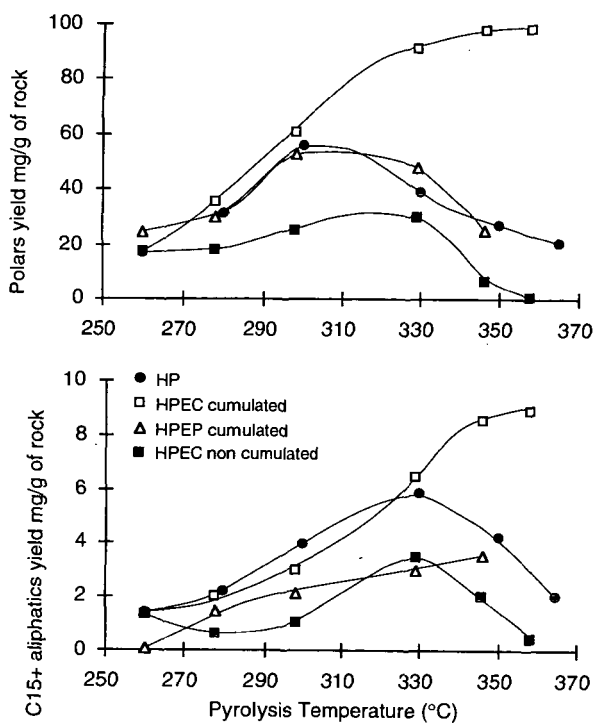
FIGURE 2 PyGCMS chromatograms of the chloroform extracted residue for each pyrolysis series